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Intercomparison study of NO_x passive diffusion tubes with chemiluminescence analysers and evaluation of bias factors

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Highlights

- Passive diffusion tubes (PDTs) are a simple method to monitor air pollutants.
- NO_2 and NO_x PDTs are influenced by factors causing bias.
- Negative bias in total NO_x capture was observed in polluted environments.
- Positive bias for PDTs was observed in PDTs exposed to wind.
- At low NO_x concentrations and when PDTs are sheltered, PDTs should perform well.

Abstract

Passive diffusion tubes (PDTs) are a cheap and simple method to monitor air pollutants. Numerous studies have investigated the performance of PDTs for NO_2 but little attention has been paid to PDTs for NO_x. The aim of this study was to evaluate the performance of NO_x PDTs in three different urban environments. Duplicate NO_x and NO_2 PDTs were co-located with chemiluminescence analysers at kerbside, urban centre and background sites in the city of Glasgow for twelve 1-week exposures. PDT measurements generally showed good temporal correlations with NO_x and NO_2 determined by the continuous analysers. However detailed evaluation showed PDT measurements were variously influenced by factors causing bias, according to individual site characteristics: positive bias in both NO_x and NO_2 PDTs due to wind-associated shortening of diffusion path; positive bias in NO_2 PDTs due to within-tube chemical reaction between NO and O_3; and, where NO concentrations were high, negative bias in NO_x PDTs assumed due to incomplete oxidation of NO by the in-cap oxidising granules. In conclusion, where ambient NO_x is low (less than a few tens of $\mu g\ m^{-3}$), and PDTs are in sheltered locations, NO_x PDTs should perform well over 1-week exposures; however substantial negative bias for NO_x PDTs is expected in polluted roadside environments for exposures of several weeks as is usually the case in ambient air quality deployment. Observations from this study suggest that sheltering PDTs from high wind is important to minimise positive bias due to wind-associated shortening of the diffusion path.

Key words: nitrogen oxides; passive samplers; diffusion tubes; air pollution monitoring

1 Introduction

The gases nitrogen dioxide (NO_2) and nitric oxide (NO) (collectively referred to as nitrogen oxides (NO_x)) play a key role in atmospheric chemistry contributing to the formation of secondary air pollutants including ozone (O_3) and peroxyacyl nitrate (PAN) (Marston, 1999). NO_2 and O_3 are powerful oxidants and have been associated with adverse health effects and mortality in epidemiological studies (Bell et al., 2005; Neurberg et al., 2007; Latza et al., 2009). NO_x concentrations are used as a tracer of traffic-related air pollution (Harrison et al., 2003) and have been found to be highly correlated with particle number concentrations (Ketzel et al., 2003; Harrison and Jones, 2005), which has been identified as an important causative agent of the health effects produced by particles. Emissions of NO_x also contribute to environmental acidification (AQEG, 2004) and the reactive nitrogen cascade (Galloway et al., 2008).

As a consequence of all the above, monitoring of NO, NO_2 and NO_x concentrations is required for the investigation of the extent of air pollution and the evaluation of measures to improve air quality. In contrast to automatic analysers which require elaborate infrastructure and maintenance, passive diffusion samplers are a cheap and simple method to measure air pollutants. They operate on the principle of molecular diffusion whereby molecules of the target species (e.g. NO_2) diffuse down the concentration gradient from the ambient concentration at the open end of the sampler to the effective zero concentration adjacent to the surface of the absorbent (triethanolamine (TEA) for NO_2) within the sampler, into which they are irreversibly trapped as nitrite.

The Palmes-type passive diffusion tube (PDT) (Palmes et al., 1976) is widely deployed across the UK and elsewhere to provide indicative measurement of average NO_2 concentration. The PDT consists of an acrylic tube of length 7.1 cm and internal diameter 1.1 cm, two opaque polyethylene caps and two stainless steel grids. The grids are place at the closed end of the PDT, coated with the absorbent. Factors affecting the performance of NO_2 PDTs have been investigated in numerous studies, reviewed recently by Cape (2009), and include:
(1) Within-tube reaction between co-diffusing NO and O_3 leading to overestimation of NO_2 concentrations. The magnitude of this bias depends on the relative concentrations of atmospheric NO and O_3 at the exposure location (Heal and Cape, 1997; Kirby et al. 2000). Although this bias can be substantially negated by using tubes of UV-transmitting material

such as quartz (Heal et al. 1999), so that UV light conditions within the tube match those in the surrounding ambient air (UV light photolyses NO_2), commercial PDTs remain constructed of non UV-transmitting material (usually acrylic).
(2) Wind turbulence at the open end of the tube causing a shortening of the effective path length and a sampler uptake rate higher than the diffusion-only uptake rate on which PDT theory is based (Campbell et al., 1994; Glasius et al., 1999; Bush et al., 2001). This leads to overestimation of NO_2 concentrations. Sheltered tubes have shown lower overestimation compared with unsheltered tubes (Kirby et al., 2000).
(3) The duration of the exposure, with PDT-derived NO_2 concentrations decreasing for longer exposure periods, i.e. 4-week and 2-week exposures yield less trapped nitrite at analysis than from the sum of constituent 1-week exposures (Heal et al., 2000, Bush et al., 2001).
(4) Preparation method: dipping the stainless steel meshes results in higher precision and NO_2 uptake than pipetting the absorbent on the meshes (Hamilton and Heal, 2004; Heal, 2008).
(5) Variation in relative humidity (and temperature) causing variation in uptake rate and in stoichiometry of conversion to nitrite at the absorbent. This has been investigated experimentally (e.g. Plaisance et al., 2004; Buzica et al., 2005) and reviewed by Cape (2009) but with no clear evidence for extent of significance under UK ambient conditions (Cape, 2009).

It is also possible to measure NO_x using Palmes-type PDTs by incorporating an oxidant just behind the mesh containing the absorbent for NO_2 which oxidises the NO to NO_2 which is then also trapped by the NO_2 absorbent. The average ambient NO in the air can be derived from the difference between co-exposed NO_2 and NO_x PDTs. However, very little attention has been paid in the literature to Palmes-type NO_x PDTs in the urban setting. The study by Vardoulakis et al. (2009) reported considerable underestimation by NO_x PDTs compared with chemiluminescence analyser measurements at two roadside and one background site in Birmingham for 4 and 5 week exposure periods but did not make detailed comment on their findings in respect of the known bias factors highlighted above.

This study reports on the comparison of NO_x PDT measurements with co-located chemiluminescence analyser in three different urban environments in the city of Glasgow, but with 1-week exposure periods to minimise potential confounding by exposure-duration negative bias.

2 Methods

2.1 Sampler characteristics and preparation

All tube components and the oxidant granules were obtained from Gradko International Ltd. In the NO_x tubes the red cap containing the grids has an open end over which is fitted an outer black cap containing the oxidant granules held in place by a further stainless steel grid (Figure 1). The NO_2 absorbent for both types of tubes was prepared by dipping the grids in a solution of 50% TEA in acetone as described by Hamilton and Heal (2004). For the NO_x tubes 0.500 ± 0.001 g of the supplied oxidant was weighed on a Sartorius MC5 balance and added to the extra black cap.

2.2 Monitoring sites and sampling strategy

Duplicates of both NO_2 and NO_x PDTs were exposed in parallel for twelve 1-week periods between 22 May and 11 August 2007 at three monitoring stations in Glasgow, UK, with different influences from primary sources. Previous unpublished worked by our research team has shown good precision (RSD <8.0 %) for duplicate exposures. All sites are in central Glasgow and are part of the national automatic air pollution network operated by the UK Department for Environment, Food and Rural Affairs. Full site details are available at www.airquality.co.uk, so only brief description is given here.

The kerbside monitoring station is located on Hope St. (55º 51' 30' N, 4º 15' 11'' W), which has an average traffic density of ~25,000 vehicles/day and is frequently congested with buses and taxis. Four-storey buildings on both sides form a symmetric street canyon. The site at St. Enoch Sq. (55º 51' 84' N, 4º 15' 45'' W), now designated urban background but previously designated urban centre, is located in a pedestrianised square and is 20 m from the nearest main road which has an average traffic density of ~20,000 vehicles/day. The third site, also designated as urban background, is located in Montrose St. (55º 51' 22', 4º 14' 44'' W) with sampling at third-storey level. Montrose St. is a four-storey street canyon containing substantial traffic which causes it to have higher NO_x concentrations than those typically expected for an urban background site, and higher in fact, on average, than the NO_x concentrations at the St. Enoch Sq. site (as demonstrated by the results from this study and from the long-term analyser records at these two sites).

At Hope St. and St. Enoch Sq. the PDTs were mounted ~3 m above the ground, on the side of the monitoring station, and on an inlet duct protruding above the monitoring station, within 0.5 m and 0.7 m, respectively, of the continuous analyser inlets. At Montrose St. the PDTs were approximately 12 m above the ground, located within a window recess, 0.2 m from the gas analyser inlet. In all cases, no additional sheltering of the tubes was provided. Three NO_x and NO_2 field blank tubes (i.e. tubes which remained capped whilst at the site) were also mounted each week.

The NO_x chemiluminescence analysers at each site are regularly maintained and calibrated (AEA, 2009) and have an uncertainty within 15% (at 95% confidence level) as required by EU Directives.

2.3 Sampler chemical analysis

After exposure, the open end of each tube was capped and the black and red cap in the NO_x tubes was changed to a conventional closed grey cap. Tubes were double wrapped in plastic bags and stored at 4 °C until analysis, within 2 weeks.

The trapped nitrite in each PDT was extracted with deionised water and quantified by the standard sulphanilamide and N-1-naphthyl ethylene diamine dihydrochloride colorimetric method described in Heal (2008) with reference to a calibration graph constructed from standard nitrite solutions. The collected mass of nitrite was converted into ambient gas concentration using rearrangement of Fick's law (Equation 1),

$$Q = D_{12}\frac{(C_1 - C_0)At}{L} \qquad \text{Equation 1}$$

where Q is the mass of trapped nitrite (ng), D_{12} is the molecular diffusion coefficient of gas 1 in gas 2 ($cm^2\ s^{-1}$) (i.e. molecular diffusion of NO_2 in air in the case of the NO_2 PDTs and molecular diffusion of NO in air for that portion of nitrite mass in NO_x tubes not accounted for by the nitrite mass in the parallel NO_2 tube), A is the cross-sectional area of the tube (cm^2), L is the length of the tube (cm), t is the length of exposure period (s), C_1 is the average concentration of the gas at the open end of the tube over the exposure period ($ng\ cm^{-3}$) and C_0 is the concentration of the gas at the absorbent, which is assumed to be zero. Values of NO_2 and NO diffusion coefficients were calculated for the mean temperature of each exposure period using the temperature-dependent formulae provided by Massman (1998), and the mean

temperature measured at the Bishopton weather station ~18 km from central Glasgow. (Data from the British Atmospheric Data Centre, www.badc.ac.uk).

Since chemiluminescence analyser data are reported to a temperature of 293 K, for comparison with the EU Limit Values and UK Air Quality Standard Objectives (Defra, 2008), all PDT-derived NO_2, NO and NO_x concentrations in this work were likewise corrected to a temperature of 293 K (Equation 2) using the average temperature T during the exposure.

$$C_{293} = C_T \frac{T}{293} \qquad \text{Equation 2}$$

2.4 Model-simulated PDT NO_2

For PDT exposures at St. Enoch Sq., where hourly average concentrations of O_3 were also available, it was possible to model the positive bias in NO_2 concentration that a NO_2 PDT would record when allowing for the within-tube reaction between NO and O_3 also present in the ambient air during an individual exposure. Details of the numerical model and its use in other PDT exposure studies have been given elsewhere (Heal and Cape, 1997; Heal et al., 1999; Heal et al., 2000). The model consists of a discretised continuity equation which includes data on diffusion and reaction for NO_2, NO and O_3. The boundary conditions at the open end of the tube are the hourly concentrations measured by the automatic analyser. For NO_2 the boundary condition at the adsorbent is modelled as an infinite sink, whereas there is no such boundary condition for NO and O_3 as these species do not complex with TEA.

2.5 Data analysis

The precision of the PDT data was assessed by calculating the % relative standard deviation (RSD) of each pair of duplicate measurements. The correlation coefficient between the duplicates was calculated to assess linearity.

Linearity of the relationship between PDT and chemiluminescence analyser values was evaluated by linear correlation between the mean concentration of a duplicate PDT pair and the average over the exposure period of the hourly concentrations measured by the co-located chemiluminescence analyser. PDT accuracy was expressed as % bias with respect to the chemiluminescence analyser, $\frac{C_D - C_A}{C_A} \times 100$, where C_D and C_A are the PDT and analyser

concentrations, respectively. Paired t-tests were used to assess whether differences in concentrations were statistically significant.

3 Results

3.1 Precision, quality assurance and limit of detection

Replicate measurements were available for 35 out of 36 NO_x PDT duplicates (1 tube was vandalised) and for all 36 NO_2 PDT duplicates. The mean (± 1 SD) RSD of duplicate measurements was 3.5 ± 3.8% for NO_x PDTs and 5.9 ± 6.9% for NO_2 PDTs. The correlation coefficients between replicates were 0.99 for NO_x tubes and 0.98 for NO_2 tubes, both highly statistically significant (p <0.001). These precision data are well within normal expectations for duplicate PDT exposures. For example, mean RSDs of 7.9% and 3.8% were reported, respectively, by Heal et al. (1999) for 4-week exposures and by Kirby et al. (2000) for 2-week exposures.

Leakage around the end caps and any possible contamination during the preparation and analysis of the tubes was tested by preparation and analysis of both laboratory blanks and field blanks. One-week equivalent NO_2 concentrations in both types of blanks were always below 2.0 µg m^{-3}. The limit of detection of the method, defined as the mean of the concentration found in the field blank tubes plus three times the SD of the blanks, was calculated to be equivalent to 6.6 µg m^{-3} NO_2.

3.2 Accuracy of the PDTs

Table 1 gives the summary statistical data for accuracy in determination of NO_x, NO_2 and NO concentrations by PDT at the three sites. Scatter plots of PDT vs. analyser concentrations for NO_x and for NO_2 are shown in Figures 2 and 3, respectively.

The relationship between NO_x concentrations derived from the PDTs and those averaged from the chemiluminescence analyser varied widely between site, with mean PDT biases of −2%, +55% and −14% at Hope St., St. Enoch Sq. and Montrose St., respectively. Paired t-tests confirmed significant differences between PDT and analyser measurements at the latter two sites but not at Hope St. (Table 1). The PDT-derived NO_2 concentrations were substantially

higher than corresponding analyser concentrations at Hope St. (mean bias +46%) and at St. Enoch Sq. (mean bias +80%), but not significantly different at Montrose St. (mean bias −2%).

The biases between the NO_2 and NO_x PDTs and analyser measurements were systematic as indicated by the highly significant correlations between the two measurement methods for both analytes at all three sites (Table 1 and Figures 2 and 3), all p values <0.01. The linearity between PDT and analyser was better for NO_2 (R values in the range 0.87-0.96) than for NO_x (R values in the range 0.73-0.87), and at Hope St. compared with the other two locations, although differences in R values for different gases and sites will also depend on the different ranges of numerical values in some of the datasets.

The measured PDT NO_2 concentrations at St. Enoch Sq. compared with the values simulated to be measured by the PDT when allowing for the within-tube reaction between co-diffusion NO and O_3 are shown in Figure 4. The model simulates a mean within-tube chemistry bias at this site of 28%, ranging between 19% and 36% across the 12 exposures. The time series shows highly significant correlation between the actual and predicted PDT NO_2 (R = 0.89, p <0.01) but with the former values being 41% higher on average than the latter.

NO concentrations derived by difference between PDT NO_x and PDT NO_2 exhibited significant negative biases of −24% and −31%, on average, at Hope St. and Montrose St., respectively, but small mean positive bias of +9% at St. Enoch Sq., (Table 1). These relative bias values hide the fact that NO concentrations varied substantially across the three sites; mean NO concentrations across all exposures at Hope St., St. Enoch Sq. and Montrose St. were 96.2 8.2 and 19.0 μg m^{-3}, respectively. Therefore the negative biases at individual exposures at Hope St. correspond to underestimates in absolute NO concentrations of several tens of μg m^{-3}.

4 Discussion

The strong correlations between PDT and analyser measurements for NO_x and NO_2 across a range of ambient concentrations indicate that the PDT methodology can track well the exposure-to-exposure changes in the concentrations of these species. The observed biases of the PDT measurements are therefore systematic in nature. As indicated in the introduction,

PDTs for NO_2 and NO_x are potentially subject to a number of biases. The sources of these biases act independently of each other so the net effect on the measured variable is additive. Inspection of the PDT-analyser comparisons presented here allow inferences on the presence and magnitudes of these biases in this study and, in fact, suggest varying PDT performance characteristics across the three sites.

The presence of a significant within-tube generation of additional NO_2 will, on its own, lead to positive bias in PDT NO_2 value, and to a similar absolute negative bias in PDT-derived NO value for that exposure, but has no effect on PDT NO_x value because the biases result from a change in the split between NO and NO_2 within total NO_x. A wind-induced diffusion-path shortening will cause the same relative positive biases in the PDT determinations of each of NO_x, NO_2 and NO. Similarly, any exposure-dependent degradation of trapped nitrite will (if following first-order behaviour) cause the same relative negative biases in the PDT determinations of each of NO_x, NO_2 and NO. A further potential source of bias is failure to oxidise all NO reaching the inner end of the tube into NO_2. This will lead to the same absolute negative bias in PDT-derived NO_x and NO, but (in the absence of other factors) no bias in the NO_2 derived from the parallel NO_2-only PDT.

Substantial positive bias (overestimation) of NO_2 by PDT was observed at St. Enoch Sq. and Hope St. (80% and 46% on average, respectively). As shown in Figure 4, overestimation amounting to 28%, on average, at St. Enoch Sq. can be accounted for by within-tube reaction between ambient NO and O_3 at that location. The additional NO_2 PDT overestimation (52% on average) is the net positive bias from wind-induced shortening of diffusion path less any exposure-duration loss of trapped nitrite. These two factors will act the same relatively on PDT NO_x measurements at this site, and in fact PDT NO_x measurements are observed to have a positive bias of 55%, on average, consistent with the bias of +52% inferred from the PDT NO_2 data (particularly allowing for the fact that values quoted are averages over 12 exposures, i.e. averages of ratios do not necessarily equal ratios of averages).

The within-tube reaction between NO and O_3 contributing positive bias to NO_2 PDT measurements at this St. Enoch Sq. site necessarily contributes negative bias to PDT-derived NO values. A +28% increase, on average, in NO_2 from within-tube chemical reaction corresponds to an additional 6.4 $\mu g\ m^{-3}$ NO_2 above the mean analyser-measured NO_2 of 22.7 $\mu g\ m^{-3}$. This in turn corresponds to the chemical conversion into NO_2 of 4.1 $\mu g\ m^{-3}$, on

average, of the mean analysed-measured NO of 8.2 μg m^{-3}, i.e. to an associated average negative bias in PDT NO measurement due to the within-tube chemical reaction factor of −50%. However, the derivation of PDT NO will also be subject to the same net positive bias from wind and exposure-duration effects as the NO_2 and NO_x PDT derivations at this site, which from above has been inferred to be ~52-55%. Since the net effect of all these factors acting on PDT NO measurement are additive, the anticipated average net bias is approximately in the range +2 to +5%, again very close to the actual observed average net bias of +9% in NO PDT measurement at St. Enoch Sq. Although interpretation of the impacts of these bias factors is fully consistent between the datasets, it is clear that the PDTs at St. Enoch Sq. were subject to substantial wind-induced bias. In a comparison of 1, 2 and 4-week exposures, Heal et al. (2000) estimated an exposure-duration dependent loss term of ~5×10^{-4} h^{-1} which yields a negative bias over 1-week exposure of ~ −8%. Applying this value to the St. Enoch Sq. exposures yields an estimate for wind-induced bias at this location of ~55-60%. Glasgow, located on the West of Scotland, is one of the most wind exposed urban areas in the UK, and the St. Enoch Sq. monitoring station is in the middle of a relatively open square, with the PDTs mounted at 3 m height without shelter on an air intake duct.

Since hourly NO and O_3 data were not available at the Hope St. and Montrose St. sites the NO_2 PDT chemistry bias at those sites cannot be exactly quantified. However, O_3 concentrations are likely to be low at the kerbside location of Hope St., where mean analyser NO and NO_2 concentrations over the 12 weeks of exposure were 96 and 66 μg m^{-3}, so within-tube chemistry relative bias for NO_2 PDTs at Hope St. will be much lower than the mean chemistry relative bias of 28% simulated at St. Enoch Sq. (Figure 4). Likewise, the higher NO and NO_2 concentrations at Montrose St. (means of 19.0 and 38.9 μg m^{-3}, respectively) than at St. Enoch Sq. (8.2 and 22.7 μg m^{-3}) will lead to lower within-tube chemistry bias to NO_2 PDT at Montrose St. From unpublished simulations of chemical biases in NO_2 PDT measurements at other urban sites in the UK that have hourly O_3, NO and NO_2, the chemical biases at Hope St. and Montrose St. are likely to be in the region of +5-10% and +10-15%, respectively.

The lack of positive bias in NO_2 and NO_x PDT measurements at Montrose St. (Table 1 and Figures 2 & 3) indicate that wind-related positive bias does not appear to be an issue at this site; as noted earlier these samplers were positioned in a sheltered second-floor window recess not subject to wind, or to air turbulence from passing traffic. The agreement, on

average, between PDT and analyser for NO_2 at Montrose St. (Table 1 and Figure 3) is the net result of the small positive chemical bias and small exposure-duration negative bias, both anticipated (as discussed above) to be of magnitude around 10%. The under-read of NO_x PDTs at Montrose St. (Figure 2) confirms the presence of a small exposure-duration negative bias. An estimate of 10% NO_2 PDT over-read due to within-tube chemical reaction corresponds to an average additional NO_2 of 3.9 μg m^{-3} on an average analyser-measured NO_2 of 39 μg m^{-3}. This in turn corresponds to an average loss of 2.5 μg m^{-3} NO, or to a negative bias due to within-tube chemistry for NO PDT of −13%. This within-tube chemistry negative bias is additive with the exposure-duration negative bias and accounts for the larger negative bias overall for the NO PDT measurements at Montrose St. compared with the NO_2 and NO_x PDT measurements. Again there is consistency in the interpretation of magnitudes of the various contributing biases in the dataset at this site.

As at St. Enoch Sq., the NO_2 PDTs at Hope St. over-read by more than can be accounted for by within-tube chemistry (Figure 3) which again indicates the presence of positive bias from wind-induced turbulence. Estimating, as above, that within-tube chemical bias to NO_2 PDTs at Hope St. was ~+5-10%, and exposure-duration negative bias was −10%, then the observed NO_2 PDT over-read of 46% implies ~45-50% positive bias due to wind turbulence at this site. This is consistent with the kerbside location of these samplers where the high density of bus and other traffic passing by within a metre or two keeps air in motion. The magnitude of positive bias from wind turbulence will apply equivalently to NO_x and NO PDT measurements at Hope St., but NO_x PDTs show no over-read on average, whilst PDT-derived NO has 24% under-read, on average, at this site (Table 1). Some NO PDT negative bias will result from the small amount of within-tube reaction anticipated between NO and O_3 and exposure-duration negative bias. However, the fact the PDT-derived NO has negative bias despite the inferred substantial wind turbulence positive bias implicates incomplete oxidation of NO to NO_2 by the oxidising granules in the NO_x PDTs for the high ambient NO conditions at this location. The curvature in the Hope St. data points in Figure 2 corresponding to exposures with highest NO_x (and NO) concentrations is consistent with greater shortfall in NO_x capture at highest NO concentrations. Continuing the estimation of effect magnitudes, the negative bias due to incomplete granule oxidation of NO must be of the order of 60% at the high NO and NO_x concentrations at Hope St. in order to account for the observations. There are also indications from the Montrose St. dataset of a small incomplete granule

oxidation of NO even for the ambient NO concentrations present at that site, although any such effect is not great.

In summary, quantitative inspection of the data has revealed the following. At Montrose St. (urban background) within-tube chemical bias is not a major factor, there is no evidence of wind-induced turbulence bias, but evidence for exposure-duration negative bias and possibly some incomplete granule oxidation of NO at the highest NO concentrations experienced at this site. Overall, NO_x PDT performance is satisfactory at this site to well within the uncertainty tolerances of ±15% and ±25% specified for continuous analyser and diffusion tube measurements, respectively (EU, 2008). At St. Enoch Sq. (urban background) there is substantial within-tube chemical positive bias for NO_2 PDTs, and consequent negative bias for NO PDTs, and clear evidence of substantial wind-induced positive bias for NO_2 and NO_x PDT measurements. Overall, however, once the various biases are recognised and deconvoluted it appears that NO_x PDTs do appropriately measure the NO_x at this site, albeit with the additional large bias associated with the net effect of large wind-induced positive bias and small exposure-duration negative bias at this site, i.e. there is expectation that if the former bias were eliminated then NO_x PDT measurement would be close to analyser values. At Hope St. (kerbside) the apparent satisfactory performance of NO_x PDTs actually arises from opposing large positive bias from wind-induced turbulence and large negative bias from failure at high NO concentrations for the granules to oxidise all NO to NO_2 at this exposed and polluted kerbside site. Therefore NO_x PDT performance was not satisfactory at this site.

The one previous study of NO_x PDTs, by Vardoulakis et al. (2009), was carried out over 4 and 5 week exposure periods at one urban background and two roadside sites in Birmingham. The negative biases of NO_x PDT to analyser concentrations were much greater than observed in this study (means of −34% for the background site and −79% and −49% for the roadside sites). One important factor contributing to the PDT negative bias not evaluated by Vardoulakis et al. is the exposure-duration dependent under-read for their much longer exposure periods, as has been previously reported (Kirby et al., 2000; Heal et al., 2000; Bush et al., 2001). As in the current study, Vardoulakis et al. (2009) observe NO_x PDT under-read at roadside sites with high ambient NO and also suggest as explanation incomplete oxidation of NO to NO_2 by the in-cap granules in high NO environments. However, the very substantial NO_x PDT under-reads for the 4 and 5 week exposures at the roadside sites also points to

additional exposure-duration dependent loss of performance of the NO oxidation granules over these extended exposure periods at polluted sites.

5 Conclusions

For 1-week exposures, the NO_x (and NO_2) PDTs were shown to have satisfactory precision and generally correlated very well with temporal changes in NO_x and NO_2 as determined by co-located continuous analysers.

However, detailed evaluation of the results showed that PDT measurements at some sites were variously influenced by factors causing bias, in particular: positive bias in NO_2 PDT values (but not in NO_x PDT values) due to within-tube chemical reaction between NO and O_3; and positive bias presumed due to wind-induced turbulence for PDTs in exposed locations, which impacts on both NO_2 and NO_x PDTs equivalently. In addition, it was evident that where NO concentrations were very high, NO_x PDT values were subject to substantial negative bias due to incomplete oxidation of NO by the in-cap oxidising granules. This factor does not impact on NO_2 PDT values.

In conclusion, where ambient NO_x is low (less than a few tens of $\mu g\ m^{-3}$) and PDTs are in sheltered locations, the NO_x PDTs should perform well, and for the right reasons, over 1-week exposures, i.e. a bias within the ± 25% data quality objective specified by the EU for indicative measurements (EU, 2008), making these devices a simple, environmentally-friendly method of assessing trends in NO_x concentrations. However, evidence discussed in this work indicates likely substantial negative bias in total NO_x capture by NO_x PDTs in exposed polluted roadside environments, particularly for exposures of several weeks, as is usually the case for ambient air quality deployment. In rural areas, the majority of NO_x is NO_2 so there is very unlikely to be any problem with incomplete oxidation of NO to NO_2 in a NO_x PDT at such locations.

Further investigation of the relative merits of locating the PDTs in shelters, and/or use of a mesh across the open end, is recommended for eliminating bias due to wind-associated shortening of the diffusion path. However the shelters and meshes should not entirely impede air movement at the entrance of the tube. Further research is required to resolve the issue of the inefficient oxidation of NO observed in the NO_x PDTs.

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Tables

Table 1: Summary of mean ±1 SD PDT and analyser concentrations and of PDT-analyser pairwise correlations and biases for each of NO_x, NO_2 and NO at the three sites. The number of exposures is 12 in each case. Bold font indicates significant result for correlation or paired t-test, with * and ** signifying $p < 0.05$ and $p < 0.01$, respectively.

		NO_x	**NO_2**	**NO**
Kerbside	Analyser mean conc. / μg m^{-3}	212.5 ± 77.8	65.7 ± 19.5	96.2 ± 38.5
(Hope St.)	PDTs mean conc. / μg m^{-3}	212.9 ± 51.1	104.9 ± 36.6	70.5 ± 17.6
	Correlation, *R*	**0.87****	**0.96****	0.41
	Mean bias (Range)	−2 % (−34 to +22 %)	+46 % (+30 to +61 %)	−24 % (−71 to +11 %)
	p-value, paired t test	0.208	**0.000**	**0.010**
Urban Centre	Analyser mean conc. / μg m^{-3}	35.1 ± 5.3	22.7 ± 4.1	8.2 ± 1.4
(St. Enoch Sq.)	PDTs mean conc. / μg m^{-3}	58.6 ± 10.2	44.0 ± 8.6	9.5 ± 4.5
	Correlation, *R*	**0.77****	**0.90****	0.51
	Mean bias (Range)	+55 % (+36 to +82 %)	+80 % (+58 to +101 %)	+9 % (−45 to +58 %)
	p-value, paired t test	**0.000**	**0.000**	0.358
Urban Background	Analyser mean conc. / μg m^{-3}	67.7 ± 9.5	38.9 ± 6.9	19.0 ± 2.6
(Montrose St.)	PDTs mean conc. / μg m^{-3}	61.4 ± 7.9	39.2 ± 5.9	14.5 ± 2.5
	Correlation, *R*	**0.73****	**0.87****	0.13
	Mean bias (Range)	−14 % (−29 to −4 %)	−2 % (−11 to +16 %)	−31 % (−53 to −11 %)
	p-value, paired t test	**0.000**	0.359	**0.000**

Figures

Figure 1: Schematic representation of the NO_x PDT.

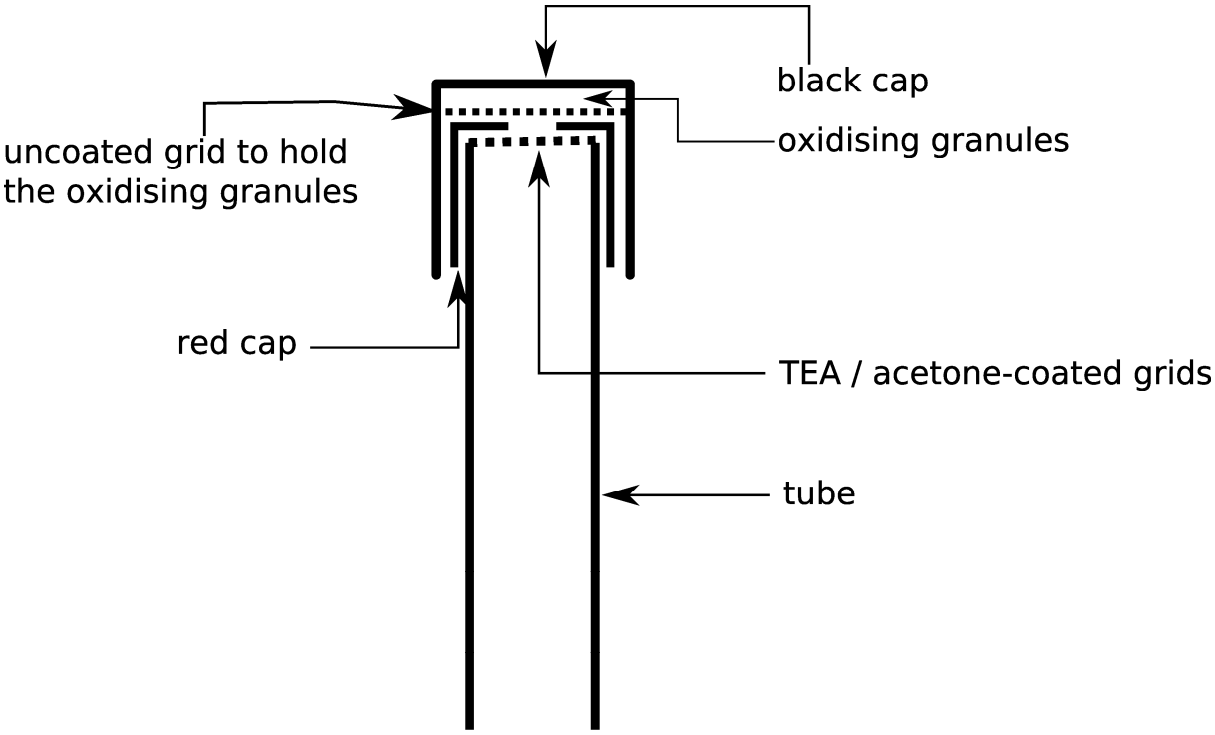

Figure 2: Scatter plot of PDT and analyser NO_x concentrations for 1-week exposures at the 3 sites.

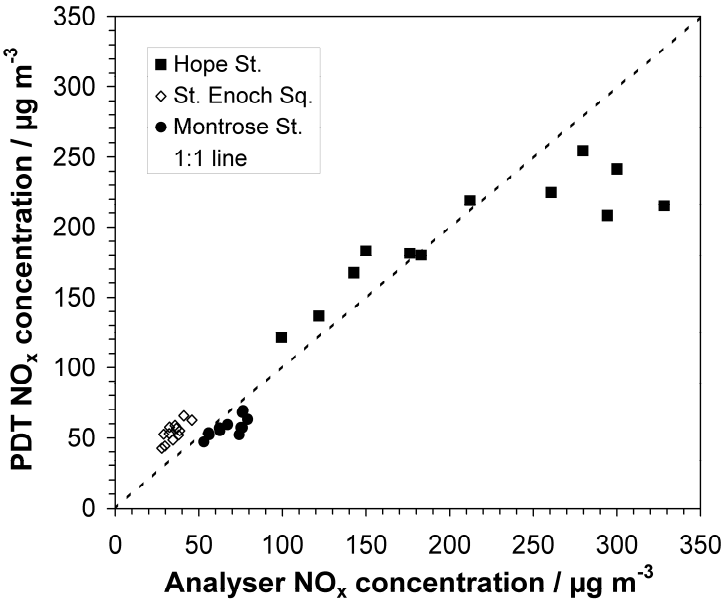

Figure 3: Scatter plot of PDT and analyser NO_2 concentrations for 1-week exposures at the 3 sites.

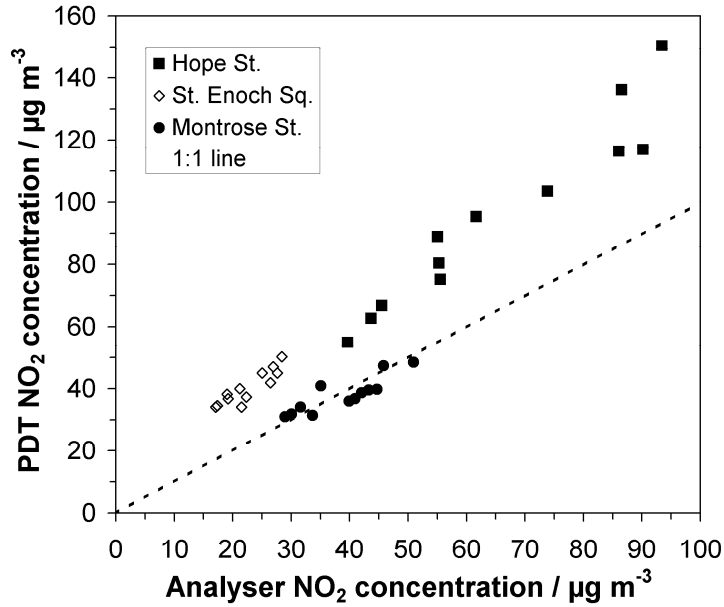

Figure 4: Time series at the St. Enoch site of analyser NO_2, PDT NO_2 and model-simulated PDT NO_2 allowing for within-tube reaction between NO and O_3 in the ambient air during the exposure.